



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification ⁵ : C23C 28/04, 16/02, 16/30 C04B 35/84, 35/80, 35/58 B32B 15/04</p>	<p>A1</p>	<p>(11) International Publication Number: WO 91/14017</p> <p>(43) International Publication Date: 19 September 1991 (19.09.91)</p>
<p>(21) International Application Number: PCT/US91/00382</p> <p>(22) International Filing Date: 22 January 1991 (22.01.91)</p> <p>(30) Priority data: 490,856 9 March 1990 (09.03.90) US</p> <p>(71) Applicant: KENNAMETAL INC. [US/US]; P.O. Box 231, Latrobe, PA 15650 (US).</p> <p>(72) Inventors: JINDAL, Prem, C. ; 615 Westchester Drive, Greensburg, PA 15601 (US). QUINTO, Dennis, T. ; 912 Beacon Valley Road, Greensburg, PA 15650 (US).</p> <p>(74) Agents: MEENAN, Larry, R. et al.; Kennametal Inc., P.O. Box 231, Latrobe, PA 15650 (US).</p>		<p>(81) Designated States: AT (European patent), AU, BE (European patent), CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), SE (European patent).</p> <p>Published <i>With international search report.</i></p>
<p>(54) Title: PHYSICAL VAPOR DEPOSITION OF TITANIUM NITRIDE ON A NONCONDUCTIVE SUBSTRATE</p> <div style="text-align: center; margin: 20px 0;"> </div> <p>(57) Abstract</p> <p>A process for physical vapor deposition of a refractory coating such as titanium nitride on a nonconductive substrate such as a ceramic substrate and the coated substrate produced thereby. The nonconductive substrate is coated by cleaning the nonconductive substrate surfaces and then depositing a first layer of a refractory metal such as titanium metal on the nonconductive substrate by physical vapor deposition. A second layer of a refractory compound such as titanium nitride is then deposited on the first layer by physical vapor deposition to produce a coated nonconductive substrate having enhanced coating adhesion.</p>		

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PHYSICAL VAPOR DEPOSITION OF TITANIUM NITRIDE ON A
NONCONDUCTIVE SUBSTRATE

FIELD OF THE INVENTION

This invention relates to a process for physical vapor deposition of a refractory coating on a nonconductive substrate and the product produced thereby. More particularly, this invention relates to a process for physical vapor deposition of a titanium nitride coating on a ceramic substrate and the product produced thereby.

DESCRIPTION OF THE RELATED ART

Various methods of physically depositing a vaporized material on a substrate, such as a base metal, are well known. For example, a gaseous specie may be physically deposited on a metal substrate by evaporation, reactive evaporation, ion-plating, and sputtering.

A typical ion-plating system for coating a substrate is described in U.S. Patent No. 3,329,601. The system includes a vacuum chamber containing a metal source, an electron source such as a filament and a substrate material supported within a substrate holder biased negatively with respect to a plasma to be generated within the chamber. In operation, the chamber is evacuated and then filled with an inert gaseous specie, such as argon. Electrons are then emitted by the filament and the metal source. Some of the electrons collide with neutral molecules in the

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plasma causing excitement and partial ionization of the gaseous species. This state of partially ionized and excited gaseous species along with free electrons is generally referred to as the plasma. The excited particles, upon returning to lower energy states, also emit photons and a visible glow is observed surrounding the substrate. Under the influence of an applied electric field, argon ions from the "glow" region are accelerated and collide with the biased substrate, effectively cleaning the substrate surface of contaminants and raising the surface temperature of the substrate. Independent heating of the substrate may also be possible prior to ion bombardment. Once the cleaning is completed, a coating metallic source, such as titanium, contained within a crucible is heated by known means causing evaporation of the coating material into the glow discharge. The ionized metal is allowed to react with a gaseous specie such as ionized nitrogen during the ion-plating process. The ion-plating process results in a uniform coating of a material such as titanium nitride, on the substrate.

Titanium and/or titanium nitride coatings have been successfully applied by physical vapor deposition to cemented carbides and tool steel substrates. Illustrative of various processes for physical vapor deposition of a coating on a cutting tool are United States Patent Nos. 4,469,489; 4,406,669; 4,539,251 and 4,337,300.

However, because ceramic substrates are inherently electrically insulating, ion-plating of a titanium nitride coating on a ceramic substrate tends to build up an electrical charge on the substrate surface. The applied bias voltage between the plasma and the ceramic substrate influences the adhesive qualities of the titanium nitride coating. Ineffective voltage biasing due to electrical charge buildup results in flaking of the coating from the ceramic

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substrate thereby producing a less than satisfactory coated ceramic.

To overcome the aforementioned problems, we have invented a novel process for physical vapor deposition of a refractory coating on a nonconductive substrate. More particularly, the present invention utilizes the ion-plating physical vapor deposition process for coating with titanium nitride any suitable nonconductive substrate such as a substrate made of a ceramic material and the like. Any suitable ceramic substrate such as a sialon (Si-Al-ON) based ceramic substrate or Si_3N_4 based ceramic substrate or Al_2O_3 based ceramic substrate including Al_2O_3 composites alloyed with or without additions of zirconia and/or other hard materials such as Silicon Carbide whiskers may be coated by the present invention. The present invention provides a process for depositing a titanium nitride coating on the nonconductive substrate by overcoming the ineffectiveness of the applied bias voltage between the plasma and the insulating substrate.

Accordingly, an object of the present invention is to provide a coating with an improved adhesion strength to a tool or article by a physical vapor deposition process, such as ion-plating.

Another object of the present invention is to provide a coated article or tool having high wear resistance, heat resistance and corrosion resistance.

Yet another object of the present invention is to provide cutting tools, wear resisting tools, wear parts and decorative articles with an improved wear resistance, heat resistance and corrosion resistance.

SUMMARY OF THE INVENTION

Briefly, according to this invention, there is provided a process of physical vapor deposition of a refractory coating, preferably a titanium nitride coating on a nonconductive substrate such as a ceramic

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substrate. The process involves cleaning the nonconductive substrate surfaces and then depositing by physical vapor deposition a first layer of a refractory metal such as titanium and then depositing a second layer of a refractory metal compound such as titanium nitride to produce a coated nonconductive substrate having enhanced coating adhesion.

The first layer increases the electrical conductivity of the nonconductive substrate such that electrical biasing in the ion-plating process becomes effective. An ion-plated titanium nitride coating on a ceramic substrate, such as a ceramic insert cutting tool, has been found to reduce flank wear, reduce the coefficient of friction between the cutting tool and a workpiece such as cast iron or nickel-based superalloy in the instance of Si-Al-ON based ceramic substrates or carbon and high temperature steels in the instance of Al_2O_3 based ceramic substrates, resulting in reduced frictional forces, and because of the chemical stability of titanium nitride, act as a diffusion barrier between the insert cutting tool and the workpiece thereby reducing tool cratering, flank wear and notching problems.

BRIEF DESCRIPTION OF THE DRAWINGS

Further features and other objects and advantages of this invention will become clear from the following detailed description made with reference to the drawings in which:

Figure 1 is a perspective view of a Kenloc style insert; and

Figure 2 is a perspective view of a Kendex style insert.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Although the present invention is described in reference to an ion-plating physical vapor deposition process for coating a nonconductive ceramic substrate, the present invention may also be used to

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coat most any suitable nonconductive substrate. The nonconductive substrate is coated by cleaning the nonconductive substrate surface and then depositing a first layer of titanium on the cleaned substrate surface. A second layer of titanium nitride is then deposited upon the first layer to produce a coated substrate having an outer layer coating exhibiting enhanced adhesion properties.

In an ion-plating physical vapor deposition process, the nonconductive substrate acts as an electrical insulator as opposed to being electrically conductive, thereby causing an electrical charge to build up on the substrate surface. The buildup of the electrical charge effectively decreases the applied bias on the substrate, which in turn results in a poor adhesive quality of a titanium nitride coating to a nonconductive substrate.

It will be appreciated that the physical vapor deposition process of the present invention may also include evaporation, reactive evaporation, ion-plating, sputtering, and magnetron sputtering and is not limited to ion-plating. However, in a preferred embodiment, the titanium nitride layer is deposited by ion-plating wherein the material to be vapor deposited is energized as positive ions by applying a negative accelerating voltage to the substrate. As used herein, ion-plating is the process occurring at the substrate and is effectively independent of the method used to generate the ions which combine to form the coating compound. For example, a variety of methods to produce metallic ions may be used for ion plating, such as thermal evaporative ion-plating, sputter ion-plating or arc evaporative ion-plating and the like.

The present invention is applicable in the production of a coated article such as a cutting tool insert having a nonconductive ceramic insert substrate. The cutting tool insert may be made by conventional

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ceramic powder processing techniques and densified by either hot pressing or pressureless sintering. The ceramic insert substrate may include Si-Al-ON based ceramic cutting inserts, Al_2O_3 based ceramic cutting inserts and other articles such as but not limited to that marketed by Kennametal Inc. under the designations KYON 2000, KYON 3000 and K090. KYON and K090 are registered trademarks of Kennametal Inc. for ceramic materials and wear resisting pieces in the form of cutting tool inserts and for wear resisting pieces consisting of hard ceramic material in the form of cutting tool inserts-namely, inserts for use in dies and tools for cutting, shaping or forming materials; respectively.

The Si-Al-ON grade cutting inserts may be either beta-prime Si-Al-ON, alpha-prime Si-Al-ON, or mixtures thereof, and may also contain a glassy phase ranging from zero to 10 percent by weight. Kyon 3000 is a beta-prime Si-Al-ON expressed by the chemical formula $\text{Si}_{6-z}\text{Al}_z\text{O}_2\text{N}_{8-z}$ wherein z has a value greater than 0 but less than 4.2. For a description of a beta-prime Si-Al-ON material reference is made to United States Patent No. 4,127,416, which is incorporated herein by reference. KYON 2000 is an alpha-prime beta-prime Si-Al-ON. Alpha-prime Si-Al-ON is expressed by the chemical formula $\text{M}_x(\text{Si},\text{Al})_{12}(\text{O},\text{N})_{16}$ wherein x is larger than 0 but not more than 2 and M is at least one selected from the group consisting of Li, Na, Ca, Mg, Y, and any rare earth element. For a complete description of mixed alpha-prime beta-prime Si-Al-ON compositions useful for cutting tool inserts, reference is made to United States Patent Nos. 4,563,433 and 4,547,470, which are incorporated herein by reference.

Among the various Al_2O_3 based ceramic cutting inserts contemplated by the present invention are cutting inserts having an Al_2O_3 microstructure in which SiC and/or refractory metal (titanium, hafnium,

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vanadium, tantalum, zirconium, and niobium) compounds (oxides, nitrides, carbides and carbonitrides) such as preferably TiC and/ or ZrO_2 particles and/or SiC or TiC whiskers dispersed therein. As disclosed in Mehrotra et al. United States Patent Application Serial No. 07/266,719 filed November 3, 1988 and assigned to Kennametal Inc., the alumina based ceramic cutting inserts may be provided with about 1.5 to 12.5 v/o (volume percent) silicon carbide whiskers and about 7.5 to 17.5 v/o zirconia dispersed in an alumina based matrix. Yet another Al_2O_3 based ceramic cutting insert is described in Mehrotra et al. United States Patent Applications Serial Nos. 07/266,721 and 07/266,735 filed November 3, 1988 and assigned to Kennametal Inc., the Al_2O_3 based cutting inserts may contain about 1.5 to 17.5 v/o silicon carbide whiskers, about 5 to 17.5 v/o zirconia, the residue of a magnesium oxide or other magnesium-oxygen compound addition, and at least 4 v/o tetragonal zirconia. Still another Al_2O_3 based cutting insert is described in Mehrotra et al. United States Patent Application Serial No. 07/266,714 filed November 3, 1988 and assigned to Kennametal Inc. The Al_2O_3 based cutting insert described in United States Patent Application Serial No. 07/266,714 may include 1.5 to 37.5 v/o silicon carbide whiskers, about 5 to 17.5 v/o zirconia, the residue of a magnesium oxide or other magnesium-oxygen compound addition, and at least 2 v/o tetragonal zirconia. Silicon carbide whiskers (SiC_w) are discontinuous, single crystal Silicon carbide (SiC) fibers and are well known in the art. The silicon carbide whiskers utilized may be of any commercially available brand which have been used in the past in the alumina based cutting inserts. It will be appreciated that a layer of TiN over a Al_2O_3 -SiC whisker reinforced composite may provide a chemically inert barrier to prevent reaction of the SiC whiskers with a steel workpiece.

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For an example of a ceramic composition including an alumina matrix having titanium carbide (TiC) whiskers dispersed therein reference is made to United States Patent No. 4,852,999 assigned to Kennametal Inc.

United States Patent No. 4,852,999 and United States Patent Applications Serial Nos. 07/266,719; 07/266,721; 07/266,735 and 07/266,714 assigned to Kennametal Inc. are incorporated herein by reference.

A preferred composition of an Al_2O_3 based ceramic insert may contain about 5-10 v/o zirconia with or without sintering aid additions, particles and/or whiskers of refractory metal compounds and/or SiC whiskers.

The Al_2O_3 based ceramic inserts are prepared by grinding the insert surfaces to a fine finish. A die penetrant of a type well known in the art may then be applied to the insert to assist in the visual evaluation of the grinding finish and check for grinding cracks. The die penetrant is preferably removed by ultrasonic cleaning for approximately one hour in a soap and warm water mixture of about 56 degrees centigrade. The insert is then baked in an air fired oven of a type typically used in drying operations to thoroughly evaporate the cleaning mixture. It will be appreciated that the use of the die penetrant and the cleaning procedure used to remove the die penetrant from the insert may be omitted and has no effect on the present invention.

Applicants have found that, by initially thoroughly cleaning the substrate surface under vacuum by heating and ion etching the substrate for a sufficient length of time to present a surface free of contaminants and then depositing a first layer of titanium on the nonconductive substrate, the aforementioned problems associated with electrical conductivity are overcome.

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A ceramic substrate is placed within a chamber, evacuated and then filled with an inert gas, such as argon. The inert gas is partially ionized and excited in the plasma as previously described. The ceramic substrate is then cleaned by heating and ion-etching. The ceramic substrate may be heated by any suitable means known in the art, such as electron bombardment. In electron bombardment, a positive potential is placed on the substrate within the chamber to attract electrons from the gaseous plasma. Under a vacuum of approximately 10^{-3} torr, the substrate is heated by the electrons striking the substrate surface thereby removing various oxides from the substrate surface. The Si-Al-ON based substrate and the Al_2O_3 based substrate are preferably heated to a temperature of approximately 400°C. It should be noted that although there is also a charge buildup during electron bombardment, the electron current density between the substrate and plasma is high enough to overcome this buildup and thus allow surface heating by electron bombardment. The substrate is then subjected to ion-etching wherein the polarity of the substrate is reversed to a negative potential to attract heavy argon ions typically used for ion-etching from the gaseous plasma to the substrate to further remove surface contaminants such as grease, dust and the like. Applicants have found, depending upon temperature, surface area of the insert to be cleaned, and degree of contamination, a ceramic substrate may be cleaned in a vacuum after a period ranging from approximately four hours to six hours. For example, the higher the heating temperature the shorter the period of cleaning required to achieve a substrate substantially free of contaminants.

A first layer of titanium is then evaporated and deposited over the cleaned ceramic substrate. The titanium is evaporated and deposited for approximately

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ten minutes by any known suitable means such as resistance heating, electron bombardment, or radio-frequency inductive heating. The deposited titanium layer increases the electrical conductivity of the ceramic substrate surface at the deposition temperature such that electrical biasing during the physical vapor deposition process becomes effective.

A second layer of titanium nitride is then deposited upon the first layer. The second layer of titanium nitride is deposited by introducing nitrogen gas into the vacuum chamber to react with the titanium present to form titanium nitride. The negative bias of the titanium coated substrate causes a resultant glow discharge to increase the kinetic energy of the depositing titanium nitride material thereby resulting in the deposition of a coating of titanium nitride of variable thickness. As a result of the present invention, excellent coating adhesion and dense coating structures may be obtained for a ceramic substrate.

The invention will be further clarified by a consideration of the following examples. Several indexable metal cutting inserts in Kennametal Si-Al-ON grades and Kennametal Al_2O_3 grades of both Kenloc and Kendex styles as shown in Figure 1 and Figure 2, respectively; were coated with titanium nitride. As shown in Figures 1 and 2 each metal cutting insert 10 has a flank face 12, a rake face 14 and a cutting edge 16 at the juncture of the flank face and the rake face. Passing through the rake face of the Kenloc style insert shown in Figure 1 is an opening 18. Kenloc and Kendex are registered trademarks of Kennametal Inc. for cutting tools having an indexable cutting insert and for carbide cutting tools, respectively.

The ceramic substrates were coated in a Balzers BAI 830 physical vapor deposition system having a vertically movable crucible. The ceramic substrates were heated under a vacuum of approximately 10^{-3} torr.

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for a period ranging from approximately three hours to six hours. Titanium was then deposited on the cleaned ceramic substrates. Titanium nitride was then deposited on the titanium coating. Next, titanium nitride coating thickness and adhesion were evaluated on the flank faces of the inserts. The coating thickness and degree of adhesion using the present invention were similar to that found in physical vapor deposition titanium nitride coated cemented carbide substrates.

EXAMPLE 1

Several ceramic metal cutting inserts, styles SNGA-433 composed of Kyon 2000 and Kyon 3000 were individually heated in separate test runs for approximately 4 hours to a temperature of approximately 400°C followed by 1/2 hour of ion etching at a pressure of approximately 10^{-3} torr in a Balzers BAI 830 system. An initial layer of titanium was then coated to the insert surface by applying an arc current of approximately 125 amps for a period of approximately five minutes to the titanium within the crucible as the crucible moved vertically within the vacuum chamber and then increasing and maintaining the arc current to approximately 200 amps for approximately five minutes. Nitrogen gas was then introduced into the system for about 80 minutes to form a titanium nitride coating on the insert surface.

Although the thickness of the titanium layer was too thin for optical microscopic measurement, the presence of the titanium layer was observed by a transmission electron microscope. The titanium nitride coating thickness was determined by the ball wear scar thickness test as set forth in Proc. 9th Int. Conf. on CVD, Electrochemical Society, Pennington, NJ, 1984, P. K. Mehrotra, D. T. Quinto and G. J. Wolfe, P. 757, which is incorporated herein by reference. The titanium nitride coating thickness was measured to be

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approximately 2-3 microns on the flank faces. The adhesion level of the coating was determined by the indentation test as set forth in Thin Solid Films, 154 (1987) 361-375 which is also incorporated herein by reference. The coating thickness and degree of adhesion using the present invention were similar to that found in physical vapor deposition titanium nitride coated cemented carbide substrates. The adhesion level was determined to be greater than or equal to 60 kg. on each sample tested.

EXAMPLE 2

Several ceramic metal cutting inserts, styles SNGA-433, composed of Kyon 2000 and Kyon 3000 were individually heated in separate test runs for approximately three hours to a temperature of approximately 400°C followed by one-half hour of ion etching at a pressure of approximately 10^{-3} torr in a Balzers BAI 830 system. An initial layer of titanium was then coated to the insert surface by applying an arc current of approximately 125 amps for a period of approximately five minutes to the titanium within the crucible as the crucible moved vertically within the vacuum chamber. Arc current was then raised to approximately 200 Amps and immediately nitrogen gas was then introduced into the system for about 85 minutes to form a titanium nitride coating on the insert surface.

The titanium nitride coating thickness was determined by the ball wear scar thickness test as set forth in Proc. 9th Int. Conf. on CVD, Electrochemical Society, Pennington, NJ, 1984, P. K. Mehrotra, D. T. Quinto and G. J. Wolfe, P. 757, which is incorporated herein by reference. The titanium nitride coating thickness was measured to be approximately 2-3 microns on the flank faces. The adhesion level of the coating was determined by the indentation test as set forth in Example 1. The adhesion was inconsistent with some flaking of the coating. The adhesion level was

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determined to be approximately less than or equal to 30 kg due to insufficiently removed surface contaminants as a result of a shorter heating cycle as well as insufficient titanium layer coverage. It is believed that surface contaminants affected the application of the titanium layer to the substrate surface and in turn the applied electrical biasing of the ion plating process.

EXAMPLE 3

Several ceramic metal cutting inserts, styles SNGA-433, composed of Kyon 2000 and Kyon 3000 were individually heated in separate test runs for approximately four hours to a temperature of approximately 400°C followed by one-half hour of ion etching at a pressure of approximately 10^{-3} torr in a Balzers BAI 830 system. An initial layer of titanium was then coated to the insert surface by applying to the titanium within the crucible as the crucible moved vertically within the vacuum chamber an arc current increasing from approximately 125 amps to 200 amps over a period of approximately two minutes and then maintained at 200 amps for approximately eight minutes. Nitrogen gas was then introduced into the system for about 80 minutes to form a titanium nitride coating on the insert surface.

The titanium nitride coating thickness was determined by the ball wear scar thickness test as set forth in Proc. 9th Int. Conf. on CVD, Electrochemical Society, Pennington, NJ, 1984, P. K. Mehrotra, D. T. Quinto and G. J. Wolfe, P. 757, which is incorporated herein by reference. The adhesion level of the coating was determined by the indentation test as set forth in Example 1. The adhesion level was determined to be greater than or equal to 60 kg.

It will be appreciated that the improved adhesive coating including a first layer of titanium and second layer of titanium nitride adherently

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deposited to a ceramic substrate such as a cutting insert has been found to reduce flank wear, and reduce the coefficient of friction between the cutting insert and a ferrous workpiece material. Moreover, because titanium nitride is chemically stable, titanium nitride has been found to act as a diffusion barrier between the cutting insert and ferrous and nickel-based workpiece materials thereby reducing tool wear problems as previously described.

EXAMPLE 4

Several ceramic metal cutting inserts, styles TNG 332T composed of approximately 73 v/o Al_2O_3 and 27 v/o TiC and known under the designation K090 as obtained from Kennametal Inc. were individually heated in separate test runs for approximately four hours to a temperature of approximately 400°C followed by one-half hour of ion etching at a pressure of approximately 10^{-3} torr in a Balzers BAI 830 system. An initial layer of titanium was then coated to the insert surface by applying an arc current of approximately 125 amps over a period of approximately five minutes to the titanium within the crucible as the crucible moved vertically upward within the vacuum chamber and then applying an arc current of approximately 200 amps for approximately five minutes as the crucible moved vertically downward within the vacuum chamber. Nitrogen gas was then introduced into the system for about 80 minutes to form a titanium nitride coating on the insert surface.

Although the thickness of the titanium layer was too thin for optical microscopic measurement, the presence of the titanium layer was observed by a transmission electron microscope. The titanium nitride coating thickness was determined by the ball wear scar thickness test as set forth in Proc. 9th Int. Conf. on CVD, Electrochemical Society, Pennington, NJ, 1984, P. K. Mehrotra, D. T. Quinto and G. J. Wolfe, P. 757, which is incorporated herein by reference. The

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titanium nitride coating thickness was measured to be approximately 3 microns on the flank faces. The adhesion level of the coating was determined by the indentation test as set forth in Thin Solid Films, 154 (1987) 361-375 which is also incorporated herein by reference. The coating thickness and degree of adhesion using the present invention were similar to that found in physical vapor deposition titanium nitride coated cemented carbide substrates. The adhesion level was determined to be greater than or equal to 45 kg. on each sample tested.

EXAMPLE 5

Several ceramic metal cutting inserts, styles SNGA-433, having approximately 2.5 v/o SiC_w , 10 v/o zirconia, 0.5 v/o magnesia and the remainder Al_2O_3 as produced in accordance with United States Patent Application Serial No. 07/266,721; were ground to a fine surface finish, visually evaluated by the use of a die penetrant, and the ultrasonically cleaned as previously described. The inserts were then individually heated in separate test runs for approximately four hours to a temperature of approximately 400°C followed by one-half hour of ion etching at a pressure of approximately 10^{-3} torr in a Balzers BAI 830 system. An initial layer of titanium was then coated to the insert surface by applying an arc current of approximately 125 amps over a period of approximately five minutes to the titanium within the crucible as the crucible moved vertically upward within the vacuum chamber and then applying an arc current of approximately 200 Amps for approximately five minutes as the crucible moved vertically downward within the vacuum chamber. Nitrogen gas was then introduced into the system for about 80 minutes to form a titanium nitride coating on the insert surface.

The titanium nitride coating thickness was determined by the ball wear scar thickness test as set

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forth in Proc. 9th Int. Conf. on CVD, Electrochemical Society, Pennington, NJ, 1984, P. K. Mehrotra, D. T. Quinto and G. J. Wolfe, P. 757, which is incorporated herein by reference. The titanium nitride coating thickness was measured to be approximately 2.6 microns on the flank faces. The adhesion level of the coating was determined by the indentation test as set forth in Example 1. The adhesion level was determined to be greater than or equal to 45 kg. on each sample tested.

EXAMPLE 6

Several ceramic metal cutting inserts, styles SNGA-433, having approximately 5.0 v/o SiC_w , 10 v/o zirconia, 0.5 v/o magnesia and the remainder Al_2O_3 as produced in accordance with United States Patent Application Serial No. 07/266,721; were ground to a fine surface finish, visually evaluated by the use of a die penetrant, and the ultrasonically cleaned as previously described. The inserts were then individually heated in separate test runs for approximately four hours to a temperature of approximately 400°C followed by one-half hour of ion etching at a pressure of approximately 10^{-3} torr in a Balzers BAI 830 system. An initial layer of titanium was then coated to the insert surface by applying an arc current of approximately 125 amps over a period of approximately five minutes to the titanium within the crucible as the crucible moved vertically upward within the vacuum chamber and then applying an arc current of approximately 200 Amps for approximately five minutes as the crucible moved vertically downward within the vacuum chamber. Nitrogen gas was then introduced into the system for about 90 minutes to form a titanium nitride coating on the insert surface.

The titanium nitride coating thickness was determined by the ball wear scar thickness test as set forth in Proc. 9th Int. Conf. on CVD, Electrochemical

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Society, Pennington, NJ, 1984, P. K. Mehrotra, D. T. Quinto and G. J. Wolfe, P. 757, which is incorporated herein by reference. The titanium nitride coating thickness was measured to be approximately 2.6 microns on the flank faces. The adhesion level of the coating was determined by the indentation test as set forth in Example 1. The adhesion level was determined to be greater than or equal to 45 kg. on each sample tested.

EXAMPLE 7

Several ceramic metal cutting inserts, styles SNGA-433, having approximately 1.5 v/o SiC_w , 10 v/o zirconia, 0.5 v/o magnesia and the remainder Al_2O_3 as produced in accordance with United States Patent Application Serial No. 07/266,721; were ground to a fine surface finish, visually evaluated by the use of a die penetrant, and then ultrasonically cleaned as previously described. The inserts were then individually heated in separate test runs for approximately four hours to a temperature of approximately 400°C followed by one-half hour of ion etching at a pressure of approximately 10^{-3} torr in a Balzers BAI 830 system. An initial layer of titanium was then coated to the insert surface by applying an arc current of approximately 125 amps over a period of approximately five minutes to the titanium within the crucible as the crucible moved vertically upward within the vacuum chamber and then applying an arc current of approximately 200 Amps for approximately five minutes as the crucible moved vertically downward within the vacuum chamber. Nitrogen gas was then introduced into the system for about 90 minutes to form a titanium nitride coating on the insert surface.

The titanium nitride coating thickness was determined by the ball wear scar thickness test as set forth in Proc. 9th Int. Conf. on CVD, Electrochemical Society, Pennington, NJ, 1984, P. K. Mehrotra, D. T. Quinto and G. J. Wolfe, P. 757, which is incorporated

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herein by reference. The titanium nitride coating thickness was measured to be approximately 2.6 microns on the flank faces. The adhesion level of the coating was determined by the indentation test as set forth in Example 1. The adhesion level was determined to be greater than or equal to 45 kg. on each sample tested.

It will be appreciated that the improved adhesive coating including a first layer of titanium and second layer of titanium nitride adherently deposited to a ceramic substrate such as a cutting insert has been found to reduce flank wear, and reduce the coefficient of friction between the cutting insert and a ferrous workpiece material. Moreover, because titanium nitride is chemically stable, titanium nitride has been found to act as a diffusion barrier between the cutting insert and ferrous and nickel-based workpiece materials thereby reducing tool wear problems as previously described.

The patents and patent applications referred to herein are hereby incorporated by reference.

Having described presently preferred embodiments of the invention, it is to be understood that it may be otherwise embodied within the scope of the appended claims.

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WHAT IS CLAIMED IS:

1. A process for the production of a coated nonconductive substrate by physical vapor deposition in which said nonconductive substrate is positioned within a vacuum chamber having a titanium source and filled with an inert gas partially ionized and excited to a gaseous plasma, said process comprising:
 - (a) cleaning said nonconductive substrate surfaces;
 - (b) depositing a first layer of titanium on said nonconductive substrate surfaces; and
 - (c) depositing a second layer of titanium nitride upon said first layer to produce a coating having enhanced adhesion on said nonconductive substrate.
2. The process for the production of a coated nonconductive substrate as set forth in Claim 1 wherein said nonconductive substrate is a ceramic.
3. The process for the production of a coated nonconductive substrate as set forth in Claim 2 wherein said ceramic substrate surfaces are cleaned by heating and ion etching said ceramic substrate under vacuum.
4. The process for the production of a coated nonconductive substrate as set forth in Claim 3 wherein said ceramic substrate surfaces are heated to at least a temperature of 400°C.

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5. The process for the production of a coated nonconductive substrate as set forth in Claim 4 wherein said nonconductive substrate surfaces are cleaned under a vacuum of approximately 10^{-3} torr.

5 6. The process for the production of a coated nonconductive substrate as set forth in Claim 5 wherein said nonconductive substrate surfaces are cleaned under said vacuum for at least three hours.

10 7. The process for the production of a coated nonconductive substrate as set forth in Claim 5 wherein said nonconductive substrate surfaces are cleaned under said vacuum for at least four hours.

15 8. The process for the production of a coated nonconductive substrate as set forth in Claim 5 wherein said heating is by high current density electron bombardment wherein a positive potential is placed on said substrate to attract electrons from said gaseous plasma to said substrate surfaces.

20 9. The process for the production of a coated nonconductive substrate as set forth in Claim 5 wherein said first layer of titanium is deposited for approximately ten minutes to increase the electrical conductivity at said nonconductive substrate surfaces.

25 10. The process for the production of a coated nonconductive substrate as set forth in Claim 5 wherein said titanium nitride is at least 2 microns thick.

30 11. The process for the production of a coated nonconductive substrate as set forth in Claim 8 wherein said physical vapor deposition process is ion-plating.

35 12. The process for the production of a coated nonconductive substrate as set forth in Claim 2 wherein in said ion-etching step a negative potential is placed on said substrate to attract ions from said gaseous plasma to said substrate surfaces.

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13. A tool insert coated by physical vapor deposition comprising:

(a) a ceramic substrate;

5 (b) a first layer of titanium deposited by physical vapor deposition on said ceramic substrate; and

(c) a second layer of titanium nitride adherently deposited on said first layer by physical vapor deposition.

10 14. The tool insert as set forth in Claim 13 wherein said titanium nitride layer is at least 2 microns thick.

15 15. The tool insert as set forth in Claim 13 wherein said tool insert is a metal cutting insert having a flank face, a rake face and a cutting edge at the juncture of said flank face and said rake face.

20 16. The tool insert as set forth in Claim 15 wherein said first layer increases the electrical conductivity of said ceramic substrate surfaces and electrical biasing of the ion-plating process to increase the adhesion level of said titanium nitride layer to said ceramic substrate surfaces to at least 60 kg in the indentation adhesion test.

25 17. The tool insert as set forth in Claim 13 wherein said ceramic substrate is an Al_2O_3 based ceramic.

18. The tool insert as set forth in Claim 13 wherein said ceramic substrate is an Al_2O_3 based ceramic having SiC whiskers dispersed therein.

30 19. The tool insert as set forth in Claim 13 wherein said ceramic substrate is an Al_2O_3 - ZrO_2 based ceramic.

35 20. The tool insert as set forth in Claim 13 wherein said ceramic substrate is an Al_2O_3 -TiC based ceramic.

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21. The tool insert as set forth in Claim 13 wherein said ceramic substrate is an Al_2O_3 - ZrO_2 based ceramic having SiC whiskers dispersed therein .

5 22. The tool insert as set forth in Claim 13 wherein said ceramic substrate is an Al_2O_3 -TiC based ceramic having TiC whiskers dispersed therein.

10 23. The tool insert as set forth in Claim 13 wherein said ceramic substrate is an Al_2O_3 - ZrO_2 based ceramic including magnesia and SiC whiskers dispersed therein.

24. The tool insert as set forth in Claim 13 wherein said ceramic substrate is selected from the group consisting of silicon nitrides and sialons.

15 25. The tool insert as set forth in Claim 13 wherein said ceramic substrate is alpha-prime sialon.

26. The tool insert as set forth in Claim 13 wherein said ceramic substrate is alpha-prime beta-prime sialon.

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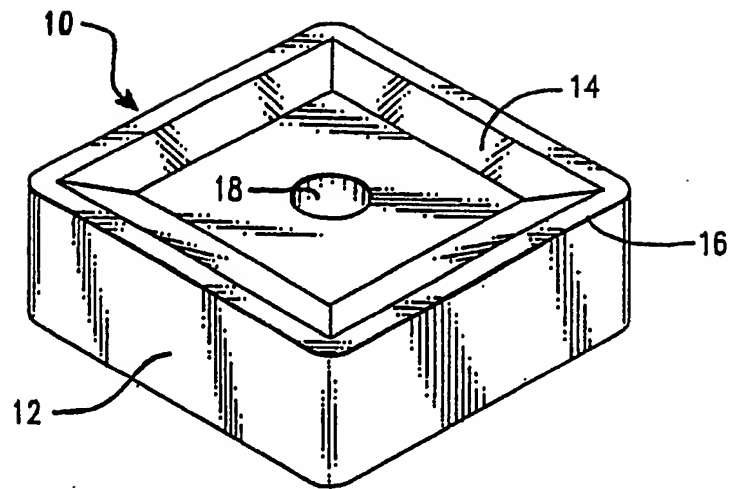


FIG. 1

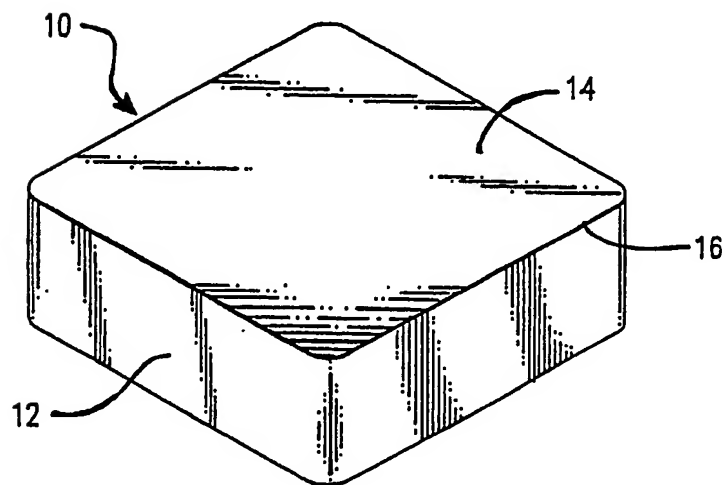
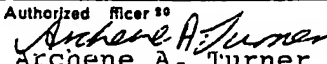


FIG. 2

INTERNATIONAL SEARCH REPORT

International Application No PCT/US91/00382

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ¹		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC (5): C23C 28/04, 16/02, 16/30; C04B 35/84, 35/80, 35/58; B32B 15/04 U.S. CL. 204/192.11; 51/307; 428/469, 472, 698, 701		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
U.S.	427/38; 204/192.11; 51/307; 428/469, 472, 698, 701	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁶		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category ⁸	Citation of Document, ¹⁰ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
Y	GB, A, 2,192,196 (BERGMANN ET AL) 06 JANUARY 1988; See entire document.	1-12
Y	Materials & Design, Vol. VI, No. 4, August/September 1985, "Titanium Nitride Coatings by Sputter Ion Plating" (COAD ET AL) pages 190-194, see page 191.	1-12
Y	US, A, 4,507,189 (DOI ET AL) 26 MARCH 1985 See the Abstract.	1-12
Y	US, A, 4,402,994 (KOBAYASHI ET AL) 06 SEPTEMBER 1983; See the Abstract and column 5, lines 19-29.	1-12
Y	US, A, 4,226,082 (NISHIDA) 07 OCTOBER 1980 See column 3, line 2, column 6, lines 27-28, column 4, line 63 and column 8, lines 11-19.	1-12
Y	US, A, 3,988,955 (ENGEL ET AL) 02 NOVEMBER 1976; See the Abstract.	1-12
Y	US, A, 3,900,592 (KENNEDY ET AL) 19 AUGUST 1975; See entire document.	1-12
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>[*] Special categories of cited documents: ¹⁵</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search ¹	Date of Mailing of this International Search Report ³	
06 MARCH 1991	04 APR 1991	
International Searching Authority ¹	Signature of Authorized Officer ¹⁰	
ISA/US	 Archene A. Turner	

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No ¹⁸
Y	US, A, 3,329,601 (MATTOX) 04 JULY 1967 See entire document.	1-12
A	US, A, 4,801,510 (MEHROTRA ET AL) 31 JANUARY 1989	13-26
Y	EP, A, 0 252 046 (SANDVIK) 07 JANUARY 1988 See entire document.	13-26
Y	US, A, 4,693,944 (SUGISAWA ET AL) 15 SEPTEMBER 1987; See column 2, lines 14-22 and column 3, line 15 and 35.	13-26
Y	EP, A, 0 247 630 (NGK SPARK PLUG CO. LTD.) 02 DECEMBER 1987; See entire document.	13-26
Y	EP, A, 0 191 554 (SUMITOMO ELECTRIC INDUSTRIES) 20 AUGUST 1986; See entire document.	13-26
Y	GB, A, 2,157,282 (SANTRADE LIMITED) 23 OCTOBER 1985; See entire document.	13-26
A	US, A, 4,539,251 (SUGISAWA ET AL) 03 SEPTEMBER 1985	
A	US, A, 4,469,489 (SARIN ET AL) 04 SEPTEMBER 1984	
A	US, A, 4,406,669 (SARIN ET AL) 27 SEPTEMBER 1983	
Y	US, A, 4,401,719 (KOBAYASHI ET AL) 30 AUGUST 1983; See entire document.	13-26
Y	JP, A, 58-64380 (DAINI SEIKOSHA KK) 16 APRIL 1983; See the Abstract.	13-26
Y	US, A, 4,337,300 (ITABA ET AL) 29 JUNE 1982 See entire document.	13-26
Y	Vacuum, Vol. 36, No. 10, 1986, "Modification of Metal Properties by Ion Plating of TiN" (ZDANOWSKI ET AL) pages 591-594, see entire document.	13-26